

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 53/94, F01N 3/28	A1	(11) International Publication Number: WO 99/39809 (43) International Publication Date: 12 August 1999 (12.08.99)
(21) International Application Number: PCT/GB99/00292 (22) International Filing Date: 28 January 1999 (28.01.99) (30) Priority Data: 9802504.2 6 February 1998 (06.02.98) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ANDREASSON, Anders [SE/SE]; Traneredsvagen 60 A, S-426 77 V. Frolunda (SE). CHANDLER, Guy, Richard [GB/GB]; 48 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). GOERSMANN, Claus, Friedrich [DE/GB]; 39 Cromwell Road, Cambridge CB1 3EB (GB). WARREN, James, Patrick [GB/GB]; 67 Burnside, Cambridge CB1 3PA (GB). (74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: SYSTEM FOR NO _x REDUCTION IN EXHAUST GASES		
(57) Abstract A system for NO _x reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO ₂ , a particulate filter, a source of reductant such as NH ₃ , and an SCR catalyst. Considerable improvements in NO _x conversion are observed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

SYSTEM FOR NO_x REDUCTION IN EXHAUST GASES

The present invention concerns improvements in selective catalytic reduction of NO_x in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO_x content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH₃ to NO_x during higher temperature operation. We believe that SCR systems have been proposed for NO_x reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO_x in a SCR system, and to improve the control of other pollutants using a SCR system.

Accordingly, the present invention provides an improved SCR catalyst system, comprising in combination and in order, an oxidation catalyst effective to convert NO to NO₂, a particulate filter, a source of reductant fluid and downstream of said source, an SCR catalyst.

The invention further provides an improved method of reducing NO_x in gas streams containing NO and particulates comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO₂, removing at least a portion of said particulates, adding reductant fluid to the gas stream containing enhanced NO₂ to form a gas mixture, and passing the gas mixture over an SCR catalyst.

Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NO_x emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO_x to N₂ by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NO₂. This may be achieved catalytically and/or by engine design or management. Desirably, the NO₂/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite SCR catalyst it is desirable to convert all NO to NO₂, whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO₂. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO_x.

The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al₂O₃ catalysts, containing 1-150g Pt/ft³ (0.035-5.3g Pt/litre) catalyst volume depending on the

NO₂/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

5 The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH₃, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of
10 compressed air was also injected around the nozzle; this provided good mixing and cooling.

The reductant fluid is suitably NH₃, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is
15 a less selective reductant than NH₃ and is presently not preferred.

Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a V₂O₅/WO₃/TiO₂ catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance
20 in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means
25 is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have
30 observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends

to reduce NOx conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO₂. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO₂ of from about 4:1 to about 1:3 by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO₂ ratios. We do not believe that it has previously been suggested to adjust the NO/NO₂ ratio in order to improve NOx reduction.

The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" at relatively low temperatures in the presence of NO₂. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NOx. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from a ceramic, but other designs of particulate trap, including woven knitted or non-woven heat-resistant fabrics, may be used.

It may be desirable to incorporate a clean-up catalyst downstream of the SCR catalyst, to remove any NH₃ or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

25

A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system, in a suitable engineered system.

30

Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

- 5 A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

Test 1 - (Comparative)

- 10 A conventional SCR system using a commercial $V_2O_5/WO_3/TiO_2$ catalyst, was adapted and fitted to the exhaust system of the engine. NH_3 was injected upstream of the SCR catalyst at varying ratios. The NH_3 was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of NH_3 gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided
15 with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow. NO_x conversions were determined by fitting a NO_x analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

- 20 A number of tests were run at different quantities of NH_3 injection, from 60% to 100% of theoretical, calculated at 1:1 NH_3/NO and 4:3 NH_3/NO_2 . It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of NH_3 at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than
25 about 70% of stoichiometric NH_3 injection, NH_3 slips through the SCR catalyst unreacted, and can cause further pollution problems.

Test 2 (Comparative)

- 30 The test rig was modified by inserting into the exhaust pipe upstream of the NH_3 injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length

(26.67cm diameter and 15.24cm length) containing 10g Pt/ft³ (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH₃ was observed in this test nor in the following test.

Test 3

The test rig was modified further, by inserting a particulate trap before the NH₃ injection point, and the tests run again under the same conditions at 100% NH₃ injection and a space velocity in the range 40,000 to 70,000 hr⁻¹ over the SCR catalyst. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

Test 4

An R49 test with 80% NH₃ injection was carried out over a V₂O₅/WO₃/TiO₂ SCR catalyst. This gave 67% particulate, 89% HC and 87% NOx conversion; the results are plotted in Figure 4.

Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Test 3 and 4 above have been confirmed.

The results have been confirmed also for a non-vanadium SCR catalyst.

CLAIMS

1. An improved SCR system for treating combustion exhaust gas containing NO and particulates, comprising in combination and in order, an oxidation catalyst effective to
5 convert at least a portion of NO in said NO_x to NO₂, a particulate trap, a source of reductant fluid and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH₃.
- 10 3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claims 1,2 or 3 wherein the particulate filter is a wall-flow filter.
- 15 5. An SCR system according to any one of the preceding claims, comprising also means to cool gases upstream of the SCR catalyst.
6. An SCR system according to claim 5, comprising also control means such that said
20 gas cooling means is activated only when a high SCR catalyst temperature is detected or conditions are determined that are expected to lead to high catalyst temperatures.
7. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
- 25 8. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced.
9. A method of reducing pollutants, including particulates and NO_x, in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to
30 convert at least a portion of NO in the gas stream to NO₂, removing at least a portion of said

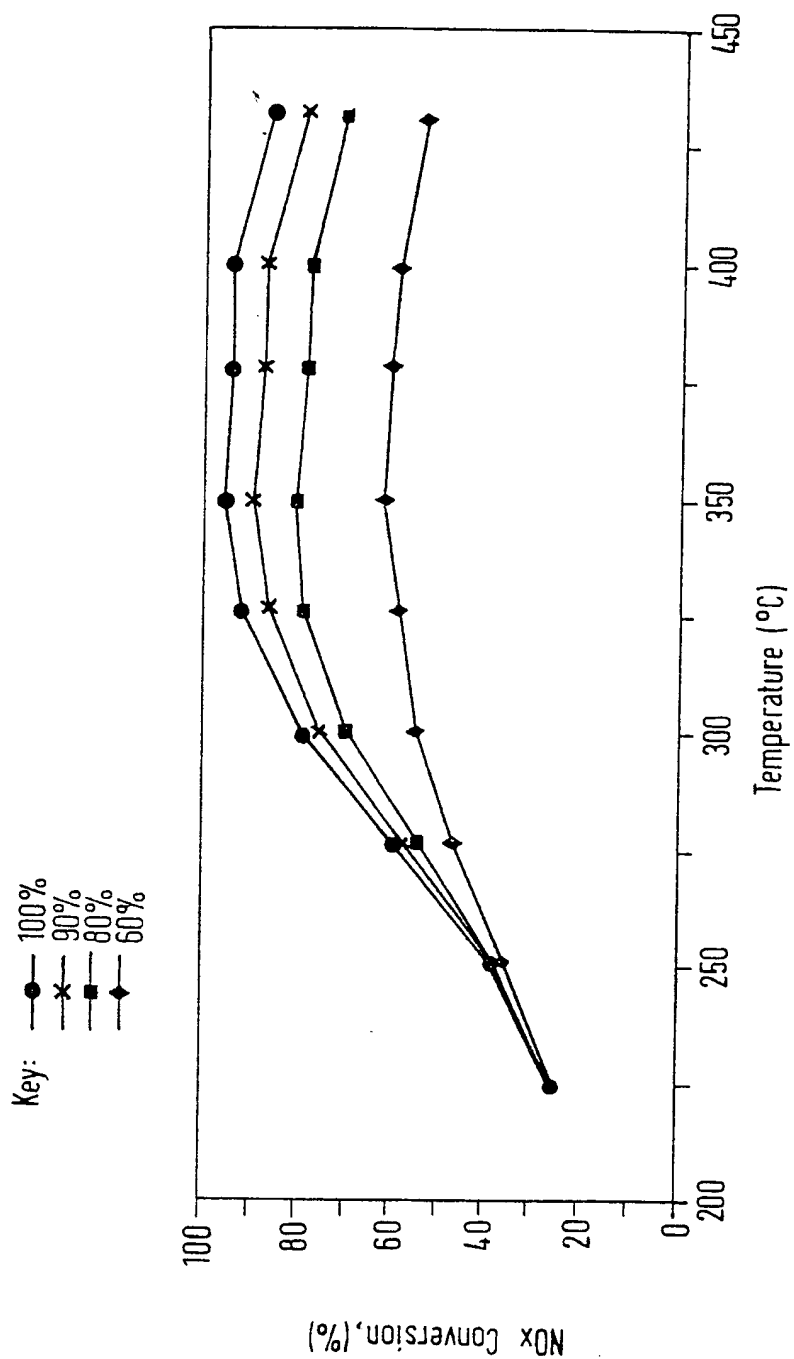
particulates, adding reductant fluid to the gas stream containing enhanced NO_2 to form a gas mixture, and passing the gas mixture over an SCR catalyst under NO_x reduction conditions.

10. A method according to claim 9, wherein said gas stream is the exhaust from a diesel,
5 GDI or CNG engine.

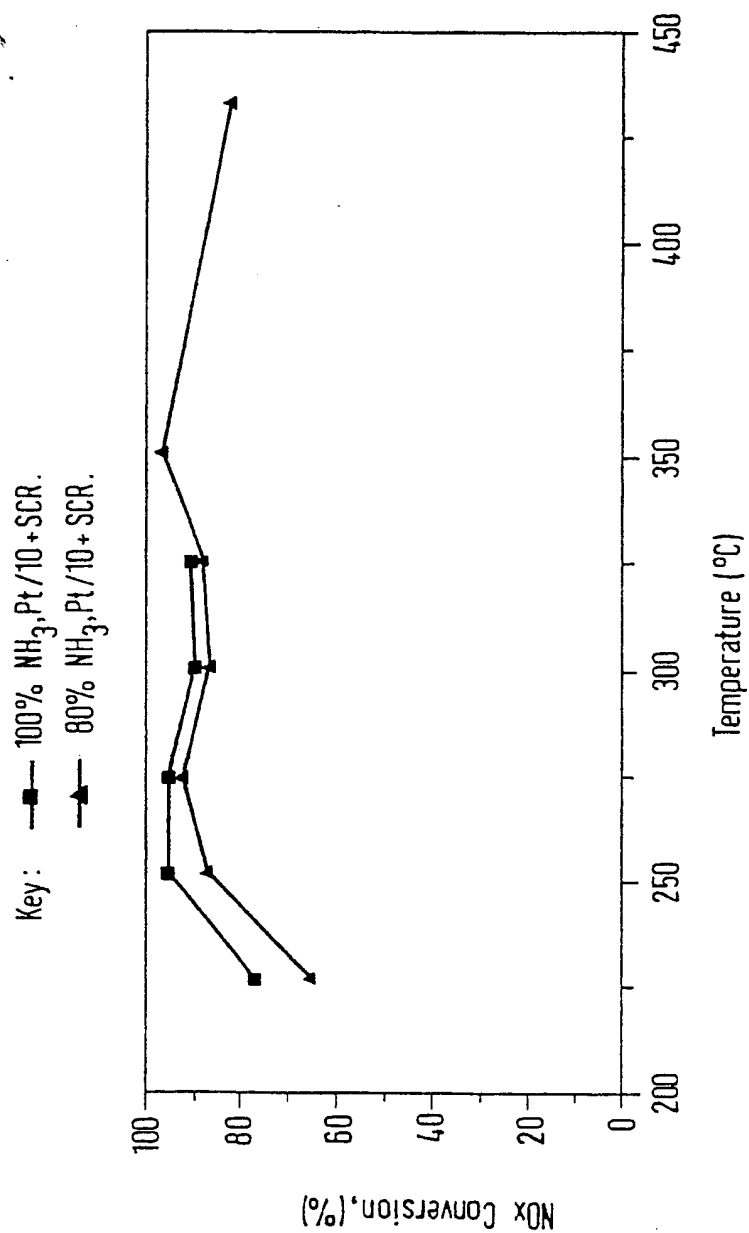
11. A method according to claim 9 or 10, wherein the gases are cooled, if necessary,
before reaching the SCR catalyst.

10 12. A method according to claim 9, 10 or 11, wherein the NO to NO_2 ratio in the gases
is adjusted to a level pre-determined to be optimum for the SCR catalyst, by oxidation of NO
over an oxidation catalyst.

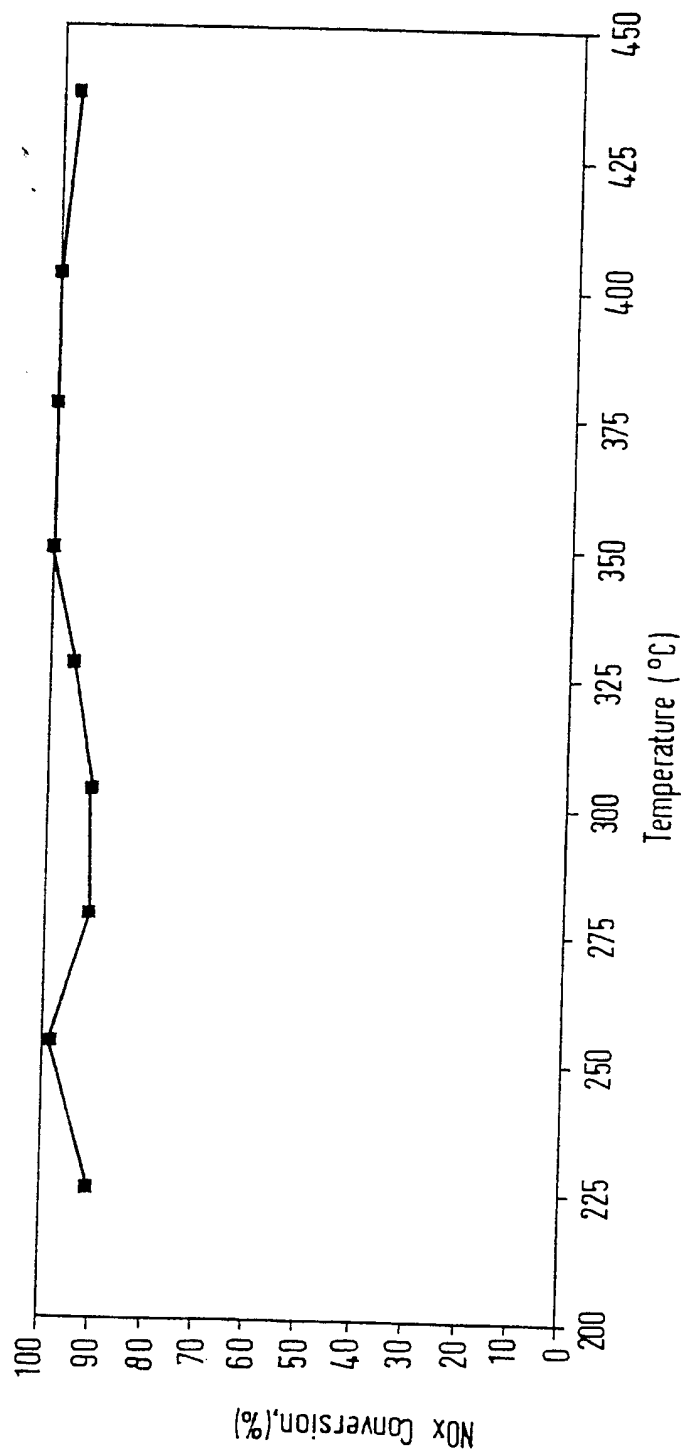
1/4



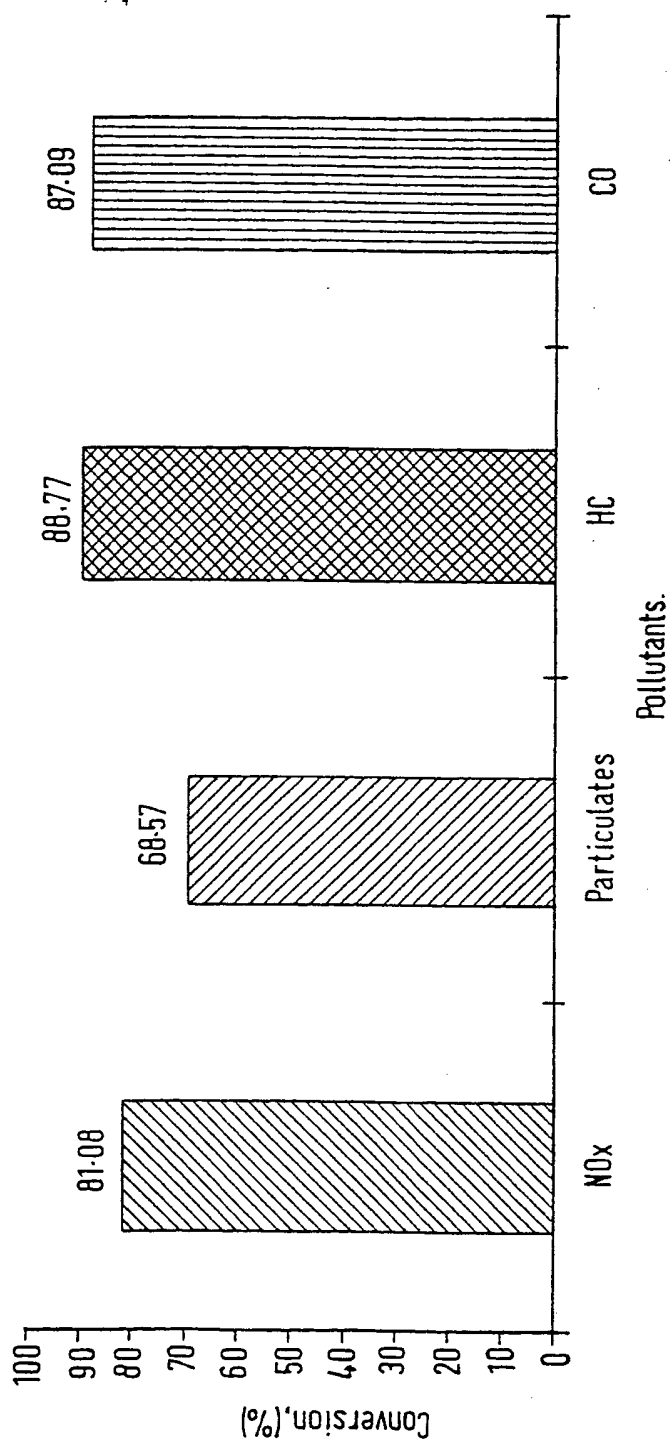
2/4



3/4



4/4



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00292

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94 F01N3/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 see column 2, line 34 - column 3, line 22 see column 16, line 33 - column 17, line 55; figure 6	1-4,7,9, 10,12
Y	EP 0 283 913 A (GRACE W R & CO) 28 September 1988 see claims 1-35; figure 1	1-4,7,9, 10,12
A	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 see claims 1-10; figure 1	1,4,7-9, 11,12
	--- -/-- ---	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 May 1999

Date of mailing of the international search report

21/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/GB 99/00292

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9710 Derwent Publications Ltd., London, GB; Class H06, AN 97-104299 XP002102630 & JP 08 338320 A (HINO MOTORS LTD) , 24 December 1996 see abstract -----	1,6-8,11
A	DE 40 32 085 A (DIDIER WERKE AG) 16 April 1992 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/GB 99/00292

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0758713 A	19-02-1997	JP 9053442 A	25-02-1997
		US 5746989 A	05-05-1998
EP 0283913 A	28-09-1988	US 4912776 A	27-03-1990
		AU 1350988 A	22-09-1988
		DE 3877229 A	18-02-1993
		JP 63236522 A	03-10-1988
EP 0341832 A	15-11-1989	US 4902487 A	20-02-1990
		AT 132940 T	15-01-1996
		DE 68925382 D	22-02-1996
		DE 68925382 T	15-05-1996
		DK 233389 A	14-11-1989
		ES 2081301 T	01-03-1996
		GR 3018800 T	30-04-1996
		IE 71167 B	29-01-1997
DE 4032085 A	16-04-1992	JP 1318715 A	25-12-1989
		BE 1006164 A	31-05-1994
		CH 681429 A	31-03-1993
		DK 171491 A	11-04-1992
		ES 2036473 B	01-03-1994
		IT 1249451 B	23-02-1995

